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"Mechanism-Imposed Limitations on the Yield of Higher Hydrocarbons from the Oxidative Coupling of Methane, and Alternate Approaches to Methane Conversion"

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13. ABSTRACT (Maximum 200 words)

The conversion of methane to higher hydrocarbons via oxidative coupling over metal oxide catalysts is the subject of intense study as a route for natural gas upgrading. Detailed study on the reaction of methane over a mixed manganese-magnesium oxide implicates a mechanism involving generation of methyl radicals at the surface, followed by radical coupling as well as other radical reactions in the gas phase as the predominant mode of carbon-carbon bond formation. Analysis of the consequences of this mechanisms suggests that there is an inherent limit on yield, including a major adverse pressure effect, that may severely impact the potential utility of this route. Among several possible approaches to circumventing this limitation, a novel class of catalyst -- transition metal-exchanged β"-alumina -- has been found to be highly active for complete oxidation of methane. Results of catalytic and characterization studies will be presented.

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MECHANISM-IMPOSED LIMITATIONS ON THE YIELD OF HIGHER HYDROCARBONS FROM THE OXIDATIVE COUPLING OF METHANE, AND ALTERNATE APPROACHES TO METHANE CONVERSION

By

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INTRODUCTION

Efficient and economic conversion of methane to more valuable products has immense potential for many applications, both for fuel and chemicals. The current benchmark, practiced in New Zealand, proceeds in three steps from methane to gasoline, via steam reformation to synthesis gas, methanol synthesis, and MTG:

$$CH_4 + H_2O \longrightarrow H_2 + CO \longrightarrow CH_3OH \longrightarrow C_nH_m + H_2O \qquad 1)$$

Intuitively, a process that starts by breaking four C-H bonds per molecule and making a C-O bond, then puts back the four H's, and finally removes the oxygen along with much of the hydrogen, might not be the most efficient route possible. Indeed, it has been estimated that processes that avoid the energy- and capital-intensive steam reformation step could be economically

much superior. However, all attempts to devise a more direct pathway from methane to methanol or higher hydrocarbons have met barriers, most often related to a fundamental problem of selectivity: since methane will usually be considerably much less reactive than products derived therefrom, simultaneously achieving good selectivity and conversion is extremely difficult.

An approach that has attracted tremendous enthusiasm over the last five years is the oxidative coupling reaction:

$$2\,CH_4 + O_2 \longrightarrow C_2H_6 + H_2O \qquad 2)$$

Equation 2) shows the reaction in its simplest possible form; in fact products include varying amounts of C_2H_6, C_2H_4 and higher hydrocarbons as well as CO and CO_2, and the reaction is catalyzed by a literally bewildering variety of main-group, transition metal and rare-earth oxides (1). A number of groups have carried out the exercise of estimating the catalyst performance that would be required for economic viability, while recognizing that there are a number of severe engineering problems that must be solved before a methane oxidative coupling process could be commercialized; the consensus seems to be in the vicinity of 25% yield (that is, conversion of methane times selectivity to higher hydrocarbon products) (2). More than a few reports in the literature meet this requirement, leading many to conclude that the selectivity problem, at least, is one that <u>can</u> be overcome for this particular approach.

However, this conclusion may be much too optimistic: our analysis suggests that the mechanism of the oxidative coupling reaction places an inherent limit on catalysis performance that in fact does <u>not</u> meet the above

requirements under practical conditions of pressure, and that cannot be overcome by means of catalyst improvement. Circumventing this limitation will require approaches that are mechanistically entirely distinct from oxidative coupling; these may be found in the realms of homogeneous, biological, or novel heterogeneous catalysts. In the following, we describe briefly the reasoning leading to the conclusion of limits on oxidative coupling, and to a new class of heterogeneous oxidation catalyst that, while not affording selective methane conversion, exhibits unusual activity for total methane oxidation with potential for applications such as methane-based fuel cells.

RESULTS AND DISCUSSION

Oxidative Coupling Mechanism and Limits

Kinetics studies were carried out using a mixed manganese-magnesium oxide in "redox" mode; that is, where methane is reacted in the absence of air with the oxidized "catalyst" (actually used as a recycled stoichiometric oxidant) that is separately regenerated by air. Materials, methods and results have previously been published (3). The key conclusion is that the reaction is initiated by abstraction of hydrogen atom at the oxide surface to generate a gas-phase methyl radical, and that much of the subsequent chemistry takes place in the gas phase. The Scheme shows the set of reactions needed to accurately model the kinetics (neglecting formation and reactions of hydrocarbons with three or more carbons). The same conclusion has been reached from other studies, most notably by direct detection and quantitation of methyl radical (4), involving a variety of

catalysts and "normal" catalytic methods (methane and air passed together over the catalyst).

Two points are of crucial importance in understanding why this mechanism limits performance. First, although formation of carbon oxide takes place at the catalyst surface, the major precursors to CO_2 – C_2H_4 and C_2H_2 – are produced to a large degree by strictly gas-phase reactions, and hence cannot be controlled by catalyst tailoring. Secondly, the reactions leading to those CO_2 precursors are <u>second-order</u> reactions, and hence become increasingly significant as the pressure is raised. Nearly all the literature reports of yields in the 25% region were obtained at methane partial pressures well below one atmosphere; but a practical process will certainly require pressures much higher than one atmosphere, and the mechanism implies this will have an adverse effect on selectivity.

By making certain extrapolations from our data, it is possible to construct a model that shows how an "ideal" oxidative coupling catalyst should behave as a function of pressure. The details of this model have been previously published (5); the results are illustrated in Figure 1, which shows: i) the predicted "best possible" performance, plotted as selectivity vs. conversion, at one atmosphere of methane; ii) the best results obtained under redox conditions with a wide variety of catalysts, agreeing well with the predicted limit (5); iii) the performance estimated to be required for economic viability at two different pressures (6); the predicted best performance at those pressures, which can be seen to fall far short of the required values.

<u>Other Approaches</u>

Since the above limitations are a direct consequence of the mechanism, it seems clear that a mechanistically distinct route is needed. Leaving heterogeneous catalysis altogether, there are promising possibilities in the realms of biological and homogeneous catalysis. For the former, the enzyme methane monooxygenase converts methane to methanol with high selectivity, although little is known about the mechanism and the obstacles to direct utilization of intact microorganisms for such a process are formidable. For the latter, a number of suggestive results have appeared in the last few years, including a platinum-based system that achieves unusual and potentially useful transformations such as oxidation of ethanol to ethylene glycol (7).

Sticking to heterogeneous catalysts, an attractive goal is to find a catalyst over which the reaction occurs at much lower temperatures such that some degree of control over mechanism may be more feasible. A class of metal oxides of potential interest in these regards are the transition metal exchanged β"-aluminas (8). These materials are unique in being the only oxides that are fast conductors of transition metal ions. Because of this weakly coordinating environment, an oxo-transition metal ion in the mobile, interlayer regions might resemble to some degree a bare metal oxo ion, possibly conferring unusual reactivity with CH_4.

We have prepared a number of these materials and tested their ability to oxidize methane in redox mode (9). Although performance for methane oxidative coupling is mediocre at best, several of the materials show surprisingly high activity for complete oxidation of methane to CO_2. For example, Mn(II)-exchanged β"-alumina exhibits significant activity at temperatures as low as 400 °C. In view of the ionic conductivity properties of

the β"-aluminas, potential applications in fuel cells based on methane or other organic fuels appear promising.

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LITERATURE CITED

(1) Hutchings, G. J., Scurrell, M. S. and Woodhouse, J. R., Chem. Soc. Rev., 18, 251 (1989); Lee, J. S. and Oyama, S. T., Catal. Rev. Sci. Eng., 30, 249 (1988).

(2) Roos, J. A., Bakker, A. G., Bosch, H., van Ommen, J. G. and Ross, J. R. H., Catal. Today, 1, 133 (1987).

(3) Labinger, J. A. and Ott, K. C., J. Phys. Chem., 91, 2682 (1987).

(4) Ito, T., Wang, J.-X., Lin, C.-H. and Lunsford, J. H., J. Am. Chem. Soc., 107, 5062 (1985); Lin, C.-H., Campbell, K. D., Wang, J.-X. and Lunsford, J. H., J. Phys. Chem., 90, 534 (1986); Campbell, K. D., Morales, E. and Lunsford, J. H., J. Am. Chem. Soc., 109, 7900 (1987).

(5) Labinger, J. A., Catal. Lett., 1, 371 (1988).

(6) Kuo, J. C. W., "Evaluation of Direct Methane Conversion to Higher Hydrocarbons and Oxygenates," Prepared for the U. S. Department of Energy under Contract No. DE-AC22-86PC90009, August 1987.

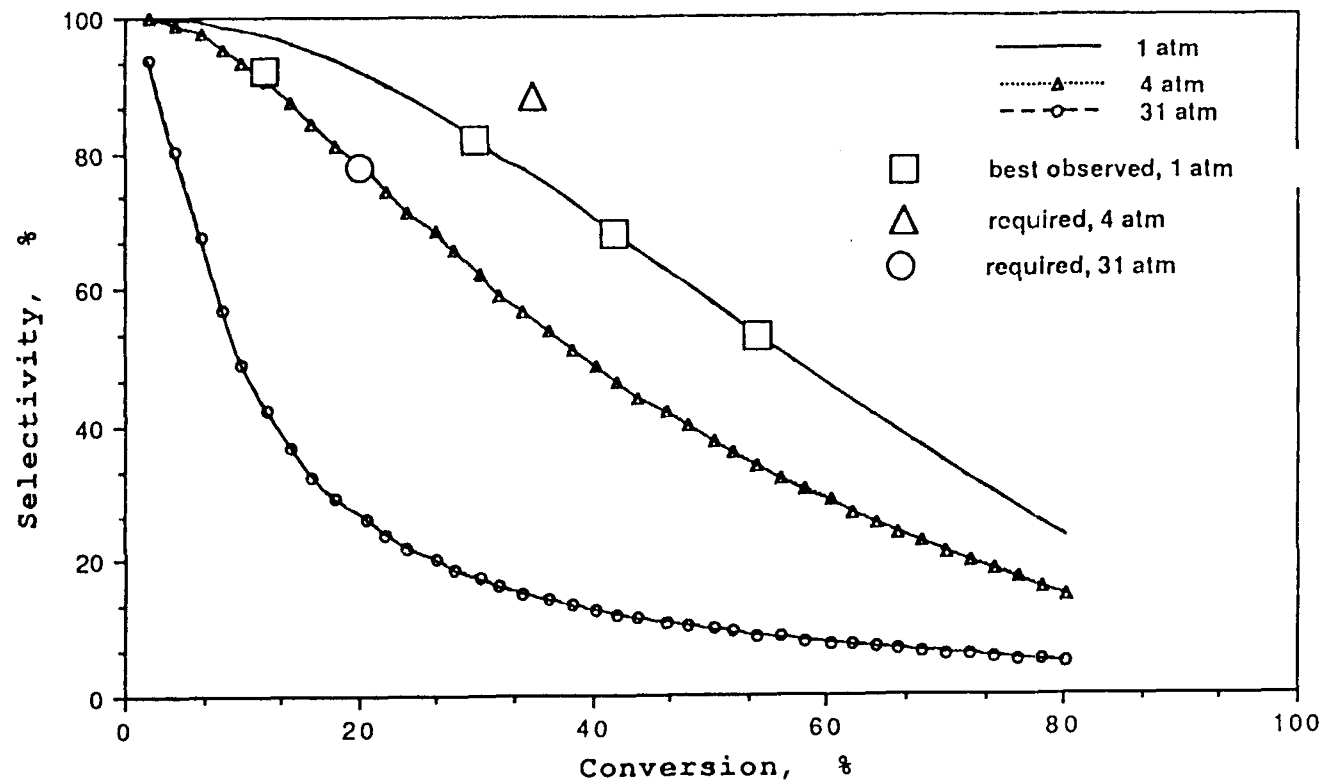
(7) Labinger, J. A., Herring, A. M. and Bercaw, J. E., J. Am. Chem. Soc., 112, 5628-9 (1990).

(8) Barrie, J. D., Dunn, B., Stafsudd, O. M. and Farrington, G. C., Solid State Ionics , 18-19, 677 (1986).

(9) Fowles, E. H., Labinger, J. A., Beauchamp, J. L. and Fultz, B., J. Phys. Chem., submitted for publication.

Caption to Figure

Figure 1. "Best" oxidative coupling performance predicted from model at three methane pressures, and comparison to observed and required values.



1 atm
4 atm
31 atm
best observed, 1 atm
required, 4 atm
required, 31 atm
Selectivity, %
Conversion, %
0
20
40
60
80
100

Scheme

$$CH_4 \xrightarrow{MO} CH_3\bullet$$

$$2\,CH_3\bullet \xrightarrow{\text{gas-phase}} C_2H_6$$

$$CH_3\bullet \xrightarrow{MO} CO_2$$

$$C_2H_6 \xrightarrow{MO} C_2H_4$$

$$C_2H_6 \xrightarrow{\text{gas-phase}} C_2H_4$$

$$C_2H_6 + CH_3\bullet \xrightarrow{\text{gas-phase}} CH_4 + C_2H_4$$

$$C_2H_4 \xrightarrow{MO} 2\,CO_2$$

$$C_2H_4 + CH_3\bullet \xrightarrow{\text{gas-phase}} CH_4 + C_2H_2$$

$$C_2H_2 \xrightarrow{MO} 2\,CO_2$$